

## ARKIV FÖR KEMI Band 2 nr 37

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## Mixed oxides with layer lattices

III. Structure of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ 

By BENGT AURIVILLIUS

With 4 figures in the text

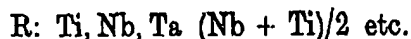
X ray studies on the compounds  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  (1) and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (2) have shown that the comparatively complicated chemical formulae of these compounds can be explained by simple layer structures being built up from  $\text{Bi}_2\text{O}_3^{2+}$  layers and perovskite layers. The unit cells are pictured schematically in Figs. 1 a and 1 c. It was found both for  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  that the symmetry was body-centered pseudo-tetragonal and that the length of the  $a$  axes had the same value (3.8 Å) while the length of the  $c$ -axis was 25 Å for  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  and 33 Å for  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ . In both structures the heavy atoms form approximately a "substructure" with a smaller body-centered tetragonal cell with  $a = 3.8$  Å and  $c = 25/5$  Å for  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  or  $c = 33/7$  Å for  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ .

The  $\text{Bi}_2\text{O}_2$  layers and perovskite layers lie perpendicular to the  $c$ -axis. Similar layer structures have been found for a number of bismuth oxicomounds (3,4,5). The common structural element in all these compounds is quadratic  $\text{Bi}_2\text{O}_2$  layers between which halides or certain radicals are inserted. This explains the fact that the  $a$  axes of all these compounds are of about the same length. For a survey see (5).

For the  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  type each perovskite layer has the composition  $(\text{CaNb}_2\text{O}_7)_n$  and the height of the layer is equal to four distances Nb—O or approximately to the height of two  $\text{E}2_1$  (perovskite) unit cells (see Fig. 1 a). A compound with a somewhat similar structure has previously been investigated by LAGERCRANTZ and SILLÉN (5). In this structure (see Fig. 1 b), beyerite  $\text{CaBi}_2\text{O}_3(\text{CO}_3)_2$ , the point positions corresponding to the positions of the Nb atoms in  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  are occupied by "rotating"  $\text{CO}_3^{2-}$  groups.

For the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  type the perovskite layers have the composition  $(\text{Bi}_2\text{Ti}_3\text{O}_{10})_n$  and the height of the layer is equal to six distances Ti—O or approximately to the height of three  $\text{E}2_1$  unit cells.

The general formula for a compound built up in a way similar to  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  but where the height of the perovskite layer enclosed between a pair of  $\text{Me}_2\text{O}_2$  layers is equal to the height of  $m$   $\text{E}2_1$  cells, will be:



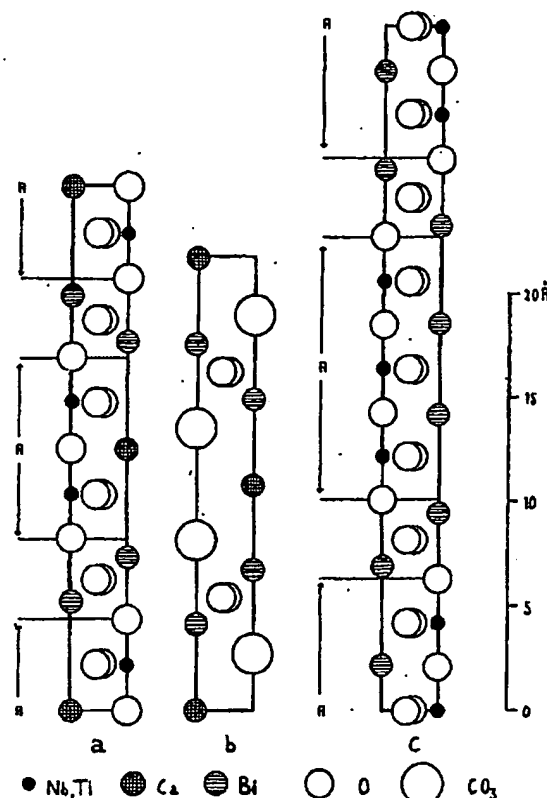
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Fig. 1. Schematic pictures of the structures of a.  $\text{CaBi}_2\text{Nb}_2\text{O}_9$ , b.  $\text{CaBi}_2\text{O}_8(\text{CO}_3)_2$  and c.  $\text{Bi}_4\text{Ti}_2\text{O}_{12}$ . The vertical lines indicate the lines  $00z$  and  $\frac{1}{2}\frac{1}{2}z$  in the unit cells. A denotes perovskitic ( $E2_1$ ) regions in the structures.

It seemed of interest to investigate whether compounds could be synthesized with  $m = 4$ . The present investigation shows that structures of the above type with  $m = 4$  exist.

Mixtures of  $\text{Bi}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{TiO}_2$ , corresponding to the composition  $\text{BaBi}_4\text{Ti}_4\text{O}_{16}$  were prepared and heated to  $1100^\circ\text{C}$ . Single crystals, thin plates, were picked out and Weissenberg photographs were taken. These could be interpreted by means of a body-centered tetragonal cell with  $a = 3.86 \text{ \AA}$  and  $c = 41.7 \text{ \AA}$ . The strong lines of the powder photographs (taken from preparations heated to  $900^\circ\text{C}$  (Au crucible) or  $1100^\circ\text{C}$  (Pt crucible)) were easily identified since they could all be described with the aid of the "sub-lattice" ( $a = 3.86$   $c = 41.7/9$ ). If the  $c$  axis were 9 fold even the weak lines could be explained (Table 3). In this way the cell edges were found to be  $a = 3.864 \text{ \AA}$  and  $c = 41.76 \text{ \AA}$ . The observed density was 7.2, which agrees fairly well with the assumption of 2 formula units/unit cell (calculated density 7.49).

The Weissenberg photographs registered  $0kl$ ,  $1kl$ ,  $hhl$  and  $h, h+1, l$ . In the Weissenberg and powder photographs there was nothing to indicate a lower Laue symmetry than  $D_{4h}-4/mmm$ . Except for the extinctions due to the body-centering,  $hkl$  occurring only for  $h+k+l = 2n$ , no systematic extinctions were found, which is characteristic of the space groups  $C_{4v}^2$ ,  $D_{2d}^{11}$  and  $D_{4h}^{17}$ . Fig. 2



Fig. 2. Patterson

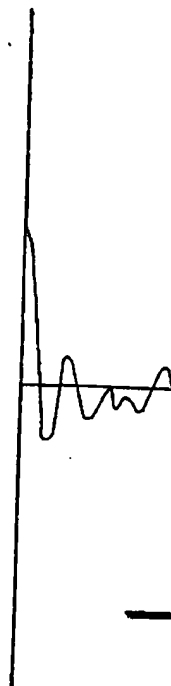


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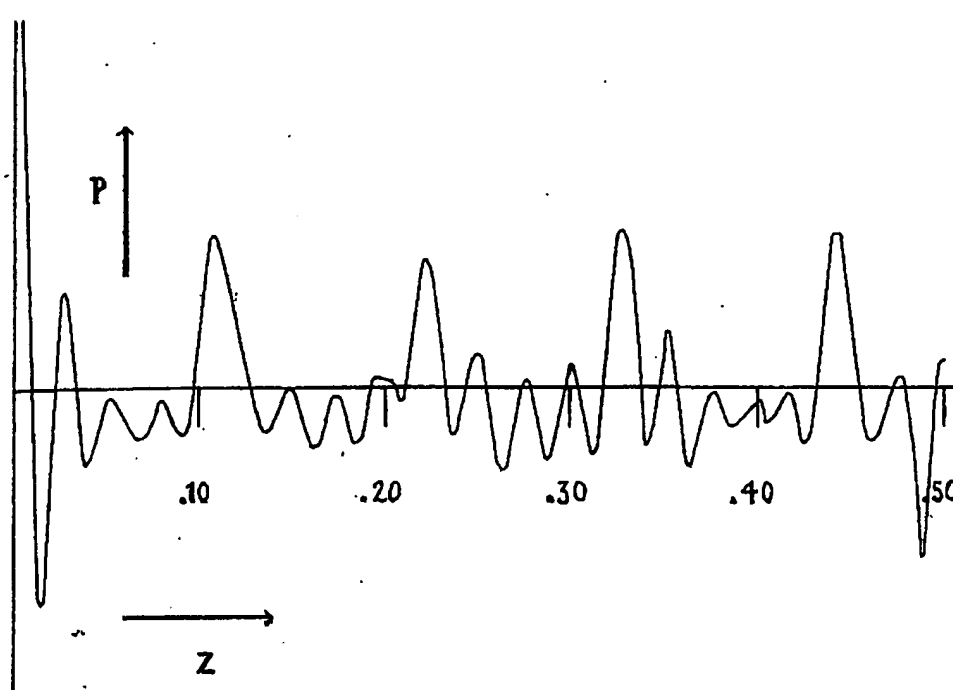


Fig. 2. Patterson Harker function of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  along  $00z$ . All observed reflexions were used for this calculation.

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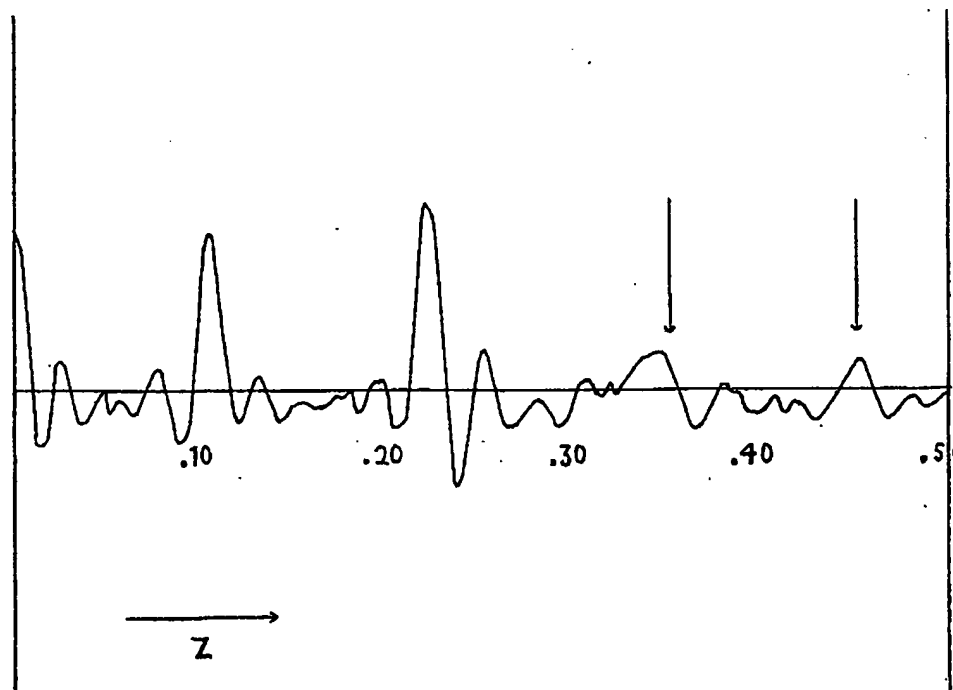


Fig. 3. Three dimensional Fourier cut along  $00z$  for  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ . The same intensity material was used as for the Patterson Harker analysis pictured in Fig. 2. The signs of the amplitudes are the same as those obtained in the structure factor calculation for Table 2. The vertical arrows correspond to the  $z_{T1}$  values actually assumed.

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shows the Patterson Harker function along 00z. For all observed reflexions the  $F^2$  values were estimated from:  $F^2 \approx I_{\text{obs.}} \frac{\sin^2 \theta}{1 + \cos^2 2\theta}$ . As expected large peaks appear at  $z \approx 1/9, 2/9, 3/9$  and  $4/9$ .

It is interesting to compare the cell dimensions found above with the ones which might be expected if the compound  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  is assumed to have a structure similar to that of  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  but with  $m = 4$ . In this case the  $a$  axis would have about the same value as found. The length of the  $c$  axis might be estimated in the following way: The  $c$  axis of  $\text{Bi}_3\text{NbTiO}_9$  ( $m = 2$  see (1)) is 25.11 Å; the value for  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  ( $m = 3$  see (2)) is 32.83, the difference is 7.72. If twice this value is added to the  $c$  axis of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  ( $m = 2$ ) the value 41.0 Å is obtained. The value actually found was, as mentioned above, 41.76 Å.

From the composition, cell dimensions, and crystal symmetry it seemed *a priori* probable that the structure of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  was the one we anticipated. Therefore, the parameters were worked out with the aid of the parameters found for

Table 1

Weissenberg photographs of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ . Cu  $K_\alpha$  radiation. For zero order photographs the regions of maximum absorption (see Wells (6)) are indicated by dotted lines. The intensities of 101, 103 and 105 have been taken from a zero order photograph, those of 1027–1049 from a first order photograph rotated around (100).

$l$	001	201	221	401	111	311	331
2		—	vw	—	—	—	vw
4		—	—	—	vw	—	vvw
6	vw	vvw	vw	—	w	—	vvw
8	m	m	w	—	m	vvw	vvw
10	m	m	w	—	st	vw	w
12	w	vvw	vw	—	vvw	—	w
14	w	—	vvw	—	w	—	—
16	st	w	m <sup>+</sup>	vvw	m	vvw	m
18	vst	m	st	w	vst	w	st
20	st	w	w	vvw	w	—	—
22	m <sup>+</sup>	vvw	vvw	vvw	vw	—	vw
24	w	vvw	vvw	vvw	vw	—	w
26	w	vvw	—	—	w	vvw	w
28	st	m <sup>+</sup>	w <sup>+</sup>	m	m	vw	—
30	w	w	w	m <sup>+</sup>	—	vw	—
32	w	w <sup>+</sup>	w	—	m	w	—
34	m	m	m <sup>+</sup>	—	m	m	—
36	st	st	st	—	m <sup>+</sup>	m	—
38	vvw	—	—	—	w	—	—
40	st	st	st	—	st	st	—
42	vvw	—	—	—	vw	—	—
44	—	—	—	—	—	—	—
46	m	m	—	—	st	—	—
48	w	m	—	—	st	—	—
50	w <sup>+</sup>	—	—	—	m	—	—
52	w <sup>+</sup>	—	—	—	—	—	—

$\text{Bi}_3\text{NbTiO}_9$   
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Table 1 (cont.)

Weissenberg photographs of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ . Cu  $K_\alpha$  radiation.

$l$	101	211	301	321	411
1	m	w	vw	vw	—
3	vvw	vvw	—	vvw	—
5	vvw	—	—	—	—
7	w	vw	vvw	w	—
9	vst	st	m	m	w
11	—	—	—	—	—
13	w	—	—	—	—
15	w <sup>+</sup>	—	vvw	—	—
17	m	vvw	vvw	—	—
19	st	vw	vvw	vvw	vvw
21	w	—	vvw	vvw	vvw
23	w	—	vvw	vvw	m
25	m <sup>+</sup>	vw	vw	vw	m <sup>+</sup>
27	st	m	w	m	—
29	m	vw	vvw	vvw	—
31	m	w	vw	vw	—
33	vw	vvw	vvw	vw	—
35	—	—	—	—	—
37	m <sup>+</sup>	m	m	—	—
39	vw	w	m	—	—
41	w	w	w <sup>+</sup>	—	—
43	w <sup>+</sup>	m	—	—	—
45	m	m <sup>+</sup>	—	—	—
47	—	—	—	—	—
49	st	—	—	—	—
51	—	—	—	—	—

$\text{Bi}_3\text{NbTiO}_9$  and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ . The positions of the heavy atoms might be expected to be: 2 Ba in 000, 4 Bi in  $\pm 00z_1$ , 4 Bi in  $\pm 00z_2$ .

The positions of the Ti and O atoms might be expected to be:

4 Ti in  $\pm 00z_3$ , 4 Ti in  $\pm 00z_4$ , 2 O in  $00\frac{1}{2}$ , 8 O in  $\pm (0\frac{1}{2}(\frac{1}{2}-z_3), \frac{1}{2}0(\frac{1}{2}-z_3))$ , 8 O in  $\pm (0\frac{1}{2}(\frac{1}{2}-z_4), \frac{1}{2}0(\frac{1}{2}-z_4))$ , 4 O in  $\pm 00(z_3+z_4)/2$ , 4 O in  $\pm 00(z_3-(z_4-z_3)/2)$ , 4 O in  $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}$   
 $z_1 \approx 1/9$   $z_2 \approx 2/9$   $z_3 \approx 0.350$   $z_4 \approx 0.450$

These atomic positions would give rise to high peaks in the Patterson-Harker plot at the same values as actually found. The calculated area ratios agree, however, with the observed ones only in as much as the biggest area is found for the peak at  $1/9$ . The reasons might be an incorrect choice of the zero level and errors in the estimation of the intensities.

The parameters were varied around the above values for different positions of the Ba atoms: 2 Ba in 000,  $00z_1$  or  $00z_2$ , 2 Ba equally distributed over  $(000+00z_1)$ ,  $(000+00z_2)$ ,  $(00z_1+00z_2)$  or  $(000+00z_1+00z_2)$ . The best agreement seemed to be for  $z_1 = 0.106 \pm 0.001$ ,  $z_2 = 0.221 \pm 0.001$ ,  $z_3 = 0.352 \pm 0.004$ ,  $z_4 = 0.452 \pm 0.004$  with 2 Ba equally distributed over  $(000+00z_1+00z_2)$ .

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Table 2

Weissenberg photographs of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ . Cu  $K_\alpha$  radiation

$$I_{\text{calc.}} = (2.5 F/f_{\text{Bi}})^2$$

$l$	$I_{\text{obs.}}$ 101	$I_{\text{calc.}}$ 101	$I_{\text{obs.}}$ 211	$I_{\text{calc.}}$ 211	$I_{\text{obs.}}$ 301	$I_{\text{calc.}}$ 301
1	m	73	w	90	vw	94
3	vvw	5.8	vvw	7.3	—	8.4
5	vvw	4.8	—	5.8	—	5.8
7	w	30	vw	31	vvw	32
9	vst	620	st	610	m	630
11	—	13	—	12	—	14
13	w	25	—	24	—	24
15	w <sup>+</sup>	62	—	60	vvw	60
17	m	94	vvw	92	vvw	90
19	st	160	vw	170	vvw	170
21	w	15	—	12	vvw	12
23	w	19	—	18	vvw	18
25	m <sup>+</sup>	120	vw	120	vw	120
27	st	320	m	320	w	320
29	m	45	vw	45	vvw	44
31	m	160	w	160	vw	160
33	vw	56	vvw	56	vvw	56
35	—	13	—	12	—	12
37	m <sup>+</sup>	300	m	300	m	300
39	vw	12	w	13	m	13
41	w	15	w	14	w <sup>+</sup>	15
43	w <sup>+</sup>	200	m	200	—	—
45	m	180	m <sup>+</sup>	180	—	—
47	—	18	—	—	—	—
49	st	250	—	—	—	—
51	—	3.6	—	—	—	—
$l$	$I_{\text{obs.}}$ 001	$I_{\text{calc.}}$ 001	$I_{\text{obs.}}$ 111	$I_{\text{calc.}}$ 111	$I_{\text{obs.}}$ 221	$I_{\text{calc.}}$ 221
2	—	—	—	0.5	vw	0.6
4	—	—	vw	4.8	—	5.3
6	vw	21	w	23	vw	24
8	m	110	m	100	w	110
10	m	62	st	280	w	98
12	w	12	vvw	6.3	vw	9.6
14	w	14	w	16	vvw	14
16	st	83	m	79	m <sup>+</sup>	81
18	vst	440	vst	480	st	450
20	st	170	w	36	w	120
22	m <sup>+</sup>	100	vw	79	vvw	92
24	w	81	vw	86	vvw	78
26	w	39	w	36	—	39
28	st	280	m	240	w	280
30	w	2.6	—	11	w	1.4
32	w	11	m	20	w	12
34	m	140	m	110	m <sup>+</sup>	140
36	st	240	m <sup>+</sup>	240	st	240
38	vvw	19	w	35	—	21
40	st	380	st	280	st	340
42	vvw	11	vw	22	—	—
44	—	3.2	—	4.8	—	—
46	m	240	st	230	—	—
48	w	69	st	46	—	—
50	w <sup>+</sup>	53	m	110	—	—
52	w <sup>+</sup>	280	—	—	—	—

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Table 3

Powder photographs of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  Cr  $K_\alpha$  radiation.

	$hkl$	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$		$hkl$	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$
alc. 0.1	0010	753	745	w		2018	5443	5440	vw
24	101	887	878	m		1025	5582	5581	w
8.4	105	1067	1058	vw		2113	5667	5669	vw
5.8	109	1489	1481	st		0028	5900	5892	vw
32	110	1758	1751	m		2018	5984	5960	m
30	0018	1927	1915	vw		2115	6088	6089	vw
14	116	2031	2018	vw		1124	6093	6089	vw
24	118	2240	2236	vw		1027	6365	6364	m
60	0018	2438	2423	m		2020	6526	6529	vw broad
90	1110	2511	2504	m		220	7032		w broad
70	1015	2572	2567	vw		222	7064	7070	w broad
12	0020	3010	2992	w		2119	7112		
18	1017	3054	3051	w		305	8099		
20	200	3516	3514	m		1031	8111	8104	vw
20	1019	3598	3600	w		2214	8114		
44	1118	3685	3681	w		2123	8376	8365	vw
60	208	3998	3996	vw		2214	8507		
56	1118	4196	4186	m		309	8521	8520	m
12	1021	4198				1130	8531		
00	2010	4269	4265	w		310	8802		
13	211	4403	4402	vw		3011	8812	8802	m
15	213	4418				312	8820		
	217	4764	4774	vw		1033	9074	9092	w broad
	1120	4768				2125	9098		
	2014	4991	5009	m		1132	9464	9484	w broad
	219	5005				2218	9470		

00 $z_2$ ). Other distributions of Ba should, however, not be excluded; as will be seen the three dimensional Fourier cut along 00 $z$  (see Fig. 3) seems to favour the following Me arrangement: 4 Bi  $\pm$  00 $z_2$  and (2 Ba + 4 Bi) equally distributed over the positions 000 and  $\pm$  00 $z_1$ .

From Table 1 it is seen that roughly for the same value of  $l$ :  $I_{001} \approx I_{201} \approx I_{221} \approx I_{401}$ ,  $I_{111} \approx I_{311} \approx I_{331}$ ,  $I_{101} \approx I_{211} \approx I_{301} \approx I_{321} \approx I_{411}$  as might be expected from the above atomic positions with atoms only on the lines 00 $z$ ,  $\frac{1}{2}\frac{1}{2}z$ ,  $0\frac{1}{2}z$  and  $\frac{1}{2}0z$ . Table 2 gives calculated and observed intensities for the rows 00 $l$ , 10 $l$ , 11 $l$ , 21 $l$ , 22 $l$  and 30 $l$ . It was found from the Weissenberg photographs that 0028  $\gg$  0030 and 1037  $>$  1039 (see Table 2) but the observed ratios do not seem to be as large as those calculated. This is more clearly seen for the rows 40 $l$  and 30 $l$  where 4028  $<$  4030 and 3037  $\geq$  3039. These discrepancies could neither be removed by small variations in the  $z$  parameters nor by assuming other distributions of the Ba atoms for the structure factor calculations. Other discrepancies found from Tables 1 and 2 are 222:224, 332:334, 0050:0052 and 1148:1152. However, for most reflexions the agreement is quite good and considering the errors which might be introduced by absorption effects and errors in the ratios  $f_{\text{Ti}}/f_{\text{Bi}}$  and  $f_{\text{O}}/f_{\text{Bi}}$  the agreement might on the whole be classified as fairly good.

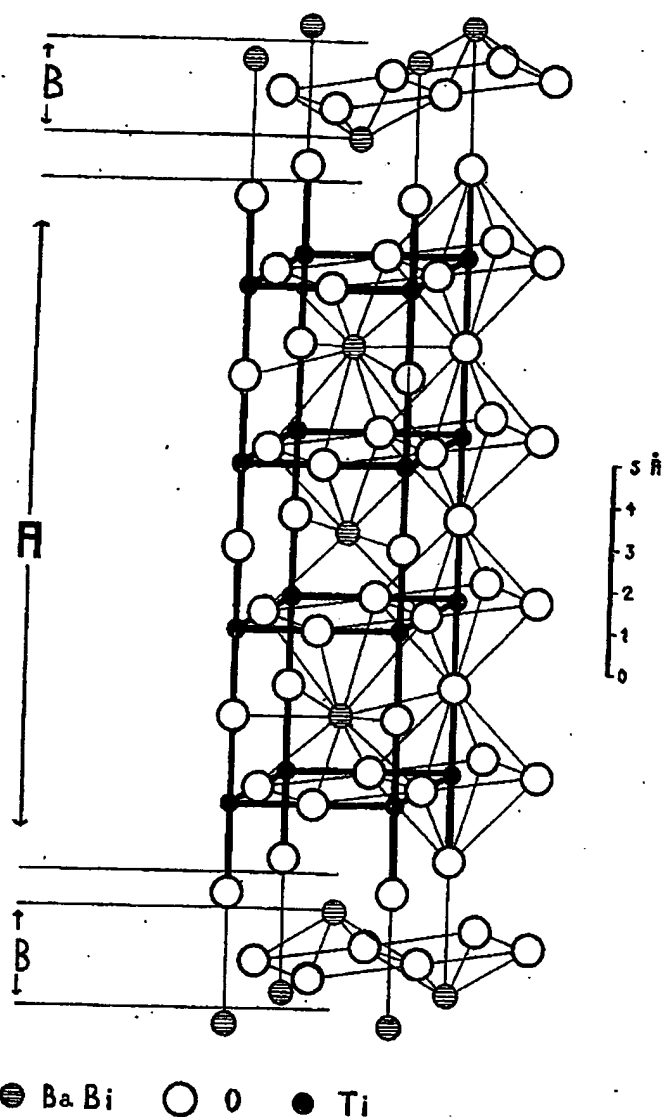
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Fig. 4. One half of the unit cell of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ . A denotes the perovskitic region and B the  $\text{Me}_2\text{O}_2$  layers.

The following structure is therefore proposed:  
 $D_{4h}^{17} - I4/mmm$   
 $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2}) +$

$2 \text{Me}_1$  in 2 (a) 000  
 $2 \text{O}_1$  in 2 (b)  $00\frac{1}{2}$   
 $8 \text{O}_2$  in 8 (g)  $0\frac{1}{2}z$ ;  $0\frac{1}{2}\bar{z}$ ;  $\frac{1}{2}0z$ ;  $\frac{1}{2}0\bar{z}$   $z = 0.048$   
 $4 \text{Ti}_1$  in 4 (e)  $00z$ ;  $00\bar{z}$   $z = 0.452$   
 $4 \text{O}_3$  in 4 (e)  $z = 0.402$

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4 Me <sub>2</sub> in 4 (e)	$z = 0.106$
8 O <sub>4</sub> in 8 (g)	$z = 0.148$
4 Ti <sub>2</sub> in 4 (e)	$z = 0.352$
4 O <sub>5</sub> in 4 (e)	$z = 0.302$
4 Me <sub>3</sub> in 4 (e)	$z = 0.221$
4 O <sub>6</sub> in 4 (d) $0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}$	

Ba and Bi equally distributed over all Me positions.

If the structure is described by means of an orthorhombic space group ( $D_{2h}^{22}$ ), as used for the structures of  $\text{Bi}_3\text{NbTiO}_9$  and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , the positions will be:  $D_{2h}^{22} - F m m m$  (000;  $\frac{1}{2}\frac{1}{2}0$ ;  $0\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}0\frac{1}{2}$ ) + 4 Me<sub>1</sub> in 4 (a) 000, 4 O<sub>1</sub> in 4 (b)  $00\frac{1}{2}$ , 16 O<sub>2</sub> in 16 (j)  $\frac{1}{4}\frac{1}{4}z$ ;  $\frac{1}{4}\frac{1}{4}\bar{z}$ ;  $\frac{1}{4}\frac{3}{4}z$ ;  $\frac{1}{4}\frac{3}{4}\bar{z}$ ;  $z = 0.048$ , 8 Ti<sub>1</sub> in 8 (i) 00 $\bar{z}$ ; 00 $\bar{z}$   $z = 0.452$ , 8 O<sub>3</sub> in 8 (i)  $z = 0.402$ , 8 Me<sub>2</sub> in 8 (i)  $z = 0.106$ , 16 O<sub>4</sub> in 16 (j)  $z = 0.148$ , 8 Ti<sub>2</sub> in 8 (i)  $z = 0.352$ , 8 O<sub>5</sub> in 8 (i)  $z = 0.302$ , 8 Me<sub>3</sub> in 8 (i)  $z = 0.221$ , 8 O<sub>6</sub> in 8 (f)  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ .

The distances (Å) and coordination will be:

O <sub>1</sub> — 8 O <sub>2</sub> = 2.78	O <sub>2</sub> — 4 O <sub>3</sub> = 2.73	Me <sub>2</sub> — 4 O <sub>2</sub> = 3.10	Ti <sub>1</sub> — O <sub>3</sub> = 2.09
O <sub>3</sub> — 4 O <sub>2</sub> = 2.84	O <sub>4</sub> — 4 O <sub>4</sub> = 2.73	Me <sub>2</sub> — 4 O <sub>3</sub> = 2.75	Ti <sub>1</sub> — 4 O <sub>2</sub> = 1.93
O <sub>3</sub> — 4 O <sub>4</sub> = 2.84	O <sub>6</sub> — 4 O <sub>6</sub> = 2.73	Me <sub>2</sub> — 4 O <sub>4</sub> = 2.61	Ti <sub>1</sub> — O <sub>1</sub> = 2.00
O <sub>5</sub> — 4 O <sub>6</sub> = 2.91			
Me <sub>1</sub> — 8 O <sub>2</sub> = 2.78	Me <sub>3</sub> — 4 O <sub>6</sub> = 2.28		Ti <sub>2</sub> — O <sub>3</sub> = 2.09
Me <sub>1</sub> — 4 O <sub>1</sub> = 2.73	Me <sub>3</sub> — 4 O <sub>5</sub> = 2.89		Ti <sub>2</sub> — 4 O <sub>4</sub> = 1.93
	(Me <sub>3</sub> — 4 O <sub>4</sub> = 3.64)		Ti <sub>2</sub> — O <sub>5</sub> = 2.09

One half of the unit cell is shown in Fig. 4.

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